



Short communication

A new hybrid redox flow battery with multiple redox couples

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H I G H L I G H T S

- ▶ Two redox couples were employed in an aqueous redox flow battery system.
- ▶ Stable cycling of over 100 cycles was demonstrated with negligible capacity fading.
- ▶ Fe/V hybrid redox flow battery represents the most efficient use of the expensive vanadium source.

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A redox flow battery using V^{4+}/V^{5+} vs. V^{2+}/V^{3+} and Fe^{2+}/Fe^{3+} vs. V^{2+}/V^{3+} redox couples in chloric/sulfuric mixed acid supporting electrolyte was investigated for potential stationary energy storage applications. The Fe/V hybrid redox flow cell using mixed reactant solutions and operated within a voltage window of 0.5–1.7 V demonstrated stable cycling over 100 cycles with energy efficiency ~80% and negligible capacity fading at room temperature. A 66% improvement in the energy density of the Fe/V hybrid cell was achieved compared with the previously reported Fe/V cell using only Fe^{2+}/Fe^{3+} vs. V^{2+}/V^{3+} redox couples.

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1. Introduction

The burgeoning rise of green and renewable energy technologies, such as solar and wind, has attracted much scientific and social interest in recent years. They are increasingly being recognized as essential components of future global energy production as awareness of environmental deterioration, resource depletion, and energy security continuously increases around the world. However, to seamlessly integrate a renewable power source with the current aging grid, an effective electrical energy storage system is needed to overcome the variable and stochastic nature of renewable sources [1]. Redox flow batteries (RFBs) have, therefore, attracted much research interest lately, mainly because of their capability to store large amounts of power or energy (up to multi-MW and -MWh, respectively). In contrast with the traditional batteries, in an RFB

the conversion between electrical energy and chemical (or electrochemical) potential occurs as the electrolytes containing active redox species flow through two electrodes separated by an ionic conducting membrane or separator. This unique mechanism gives the RFBs unparalleled advantages over other secondary battery systems, such as the separation of power and energy, long service life, easy thermal management, quick response, and capability to withstand power supply fluctuation.

Since the invention of the Fe/Cr redox flow battery in 1975 at the National Aeronautics and Space Administration (NASA) [2], the redox flow battery has undergone continuous development. A number of other redox chemistries were reported, including V^{2+}/V^{3+} vs. $Br^-/ClBr_2$ [3–5], Br_2/Br^- vs. S/S^{2-} [6,7], Br^-/Br_2 vs. Zn^{2+}/Zn [8,9], Ce^{4+}/Ce^{3+} vs. V^{2+}/V^{3+} [10], Fe^{3+}/Fe^{2+} vs. Br_2/Br^- [11], Mn^{2+}/Mn^{3+} vs. V^{2+}/V^{3+} [12], Fe^{3+}/Fe^{2+} vs. Ti^{2+}/Ti^{4+} [13], and others [14]. Among them, GEN 2Fe/Cr RFB [15] and all vanadium flow batteries (VRBs) [16–19] are probably the most researched and promising systems; both were invented and developed in the 1980s in efforts

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to alleviate the severe cross-contamination encountered in the original Fe/Cr system.

While significant progress was made in advancing RFBs with the demonstration of multi-MWh VRB systems [20] and the market-available Fe/Cr RFB system [21], the current technologies cannot meet all of the performance and cost-requirement matrices for broad market penetration. One of the main challenges facing RFBs is the intrinsically low energy density compared with other secondary energy storage systems such as lithium-ion batteries. With the voltage limitation of aqueous systems, this issue is tackled mainly by increasing the concentration of active species used in the electrolyte in previous research [22], which was often hindered by the solubility and stability issues of the active redox ions in the electrolyte solutions. In the field of solid state energy storage systems, the need for high energy and high power density has spurred research and development of multi-electron reaction materials as electrodes [23]. The rationale behind the design of the multi-electron electrode lies in Equation (1) for energy density (E_d), in which M is the unit weight (or volume), F is the Faraday constant, E_i^0 is the electromotive force of each redox reaction, and n_i is the number of electrons transferred per mole of reactants in each redox reaction. Clearly, more electron transfer results in a higher energy density [23].

$$E_d = \frac{\sum n_i F E_i^0}{\sum M_i} \quad (1)$$

In an aqueous RFB system, multiple electron transfer from a single element is probably difficult to realize due to the narrow voltage window limited by water electrolysis. However, it is possible to employ multiple electrons from different elements. The energy density (based on electrolyte only) of an RFB utilizing multiple electrons thus can be expressed as in Equation (2), which is similar to Equation (1).

$$E_d = \frac{\sum C_i V_{\text{tank}} F E_i^0}{V} \quad (2)$$

In Equation (2), energy density E_d is expressed in unit volume V (including both catholyte and anolyte), where C_i is the minimal concentration of all active species participating in the oxidation or reduction reaction i , E_i^0 is the voltage of each redox reaction, and V_{tank} is the half-cell electrolyte volume containing active specie C_i . From Equation (2), introducing multiple redox reactions with suitable voltage ranges therefore will improve the energy density of the RFB systems. Herein we report the electrochemical performance of a hybrid Fe/V RFB system utilizing both $\text{Fe}^{2+}/\text{Fe}^{3+}$ and $\text{V}^{4+}/\text{V}^{5+}$ redox couples in catholyte and a $\text{V}^{2+}/\text{V}^{3+}$ redox couple in anolyte.

2. Experimental

The electrolyte was prepared by dissolving VOSO_4 (Sigma–Aldrich, 99%) and FeCl_2 (Sigma–Aldrich, 98%) in concentrated HCl (Sigma–Aldrich, 37%) at room temperature for the Fe/V redox flow battery test, which yielded active iron and vanadium concentrations of 1.5 M respectively with 1.5 M sulfate and 6.8 M chloride ions in the final electrolyte, hereafter denoted as the 1.5Fe/V/S–6.8Cl. Cyclic voltammetry (CV) was carried out in 1.5Fe/V/S–6.8Cl electrolyte to identify redox couples and electrochemical reversibility using a Solartron 1287 potentiostat (Solartron Analytical, USA). A glassy carbon electrode (CH Instruments, USA) and Ag/AgCl electrode (CH Instruments, USA) were used as the working and reference electrode respectively, while a platinum flag served as the counter electrode. Various scan rates were used during the test.

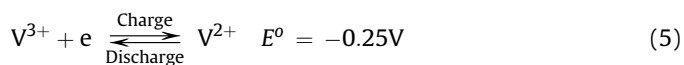
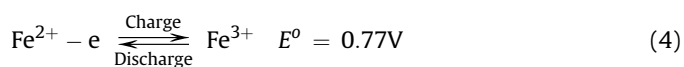
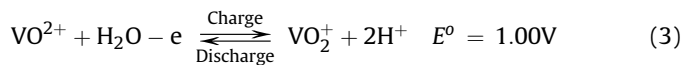
The cell performance was tested using an in-house designed flow cell system, which consists of a single cell connected with two

Pyrex® glass beaker reservoirs through a peristaltic pump (Cole-Parmer, USA) and Viton® tubing [24]. In each half cell, graphite felt (SGL Carbon Group, Germany) served as a porous electrode which was settled in a groove on a non-porous graphite current collector plate with one inlet and one outlet connections. The depth of the groove in the graphite plates was designed to maintain a 10% compression on the encapsulated graphite felt. The apparent area (i.e., the area in contact with the membrane) of the graphite felt was 10 cm^2 ($2 \times 5 \text{ cm}$); it was oxidized in air at 400°C for 6 h prior to the test to improve the electrochemical activity and hydrophilicity. Before the cell assembly, the Nafion® NR-212 membrane was soaked in deionized water for more than 24 h at ambient temperature.

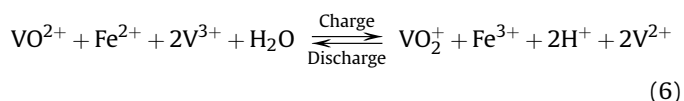
The electrochemical performance of the Fe/V flow battery was evaluated with a constant current method using a potentiostat/galvanostat (Arbin Instruments, USA). Each half-cell reservoir consisted of 1.5Fe/V/S–6.8Cl mixed acid solution as both positive and negative electrolyte, which was circulating through the graphite felt electrode at a flow rate of 20 mL min^{-1} . Each half-cell reservoir was purged with nitrogen gas and then sealed preceding the electrochemical test to minimize the oxidation of the active species. The flow cell was cycled in the voltage window between 0.5 V and 1.7 V at a constant current density of 50 mA cm^{-2} .

3. Results and discussion

As shown in Fig. 1(a), a cyclic voltammogram (CV) was first performed on the 1.5Fe/V/S–6.8Cl electrolyte to investigate the available redox reactions and their reversibility and kinetics. The CV tests were carried out using glassy carbon electrodes at ambient temperature with a scan rate of 10 mV s^{-1} . The current density was normalized to the geometrical area of the working electrode. As in our previous work on the V/V mixed acid and Fe/V system [22,24,25], a combination of three redox couples ($\text{V}^{2+}/\text{V}^{3+}$, $\text{Fe}^{2+}/\text{Fe}^{3+}$, and $\text{V}^{4+}/\text{V}^{5+}$) were identified in Fig. 1(a), which correspond to the following redox reactions in Equations (3)–(5).



Due to lack of an additional redox couple on the negative side, a double volume is used for the negative electrolyte (reaction (5)). The overall cell reaction can be written as Equation (6)



Based on the CV results of the $\text{V}^{4+}/\text{V}^{5+}$ vs. $\text{V}^{2+}/\text{V}^{3+}$ and $\text{Fe}^{2+}/\text{Fe}^{3+}$ vs. $\text{V}^{2+}/\text{V}^{3+}$ redox couples in the sulfate–chloride mixed acid electrolyte, a hybrid RFB system can be constructed with two similar equilibrium cell potentials to that of the V/V and Fe/V redox flow batteries.

The electrochemical cycling performance of the RFB system based on the $\text{V}^{4+}/\text{V}^{5+}$ vs. $\text{V}^{2+}/\text{V}^{3+}$ and $\text{Fe}^{2+}/\text{Fe}^{3+}$ vs. $\text{V}^{2+}/\text{V}^{3+}$ redox couples in the sulfate–chloride mixed acid electrolyte was then tested with a lab-made flow cell within the voltage window of 0.5–1.7 V at 50 mA cm^{-2} current density with an NR-212 membrane as described in the Experimental section.

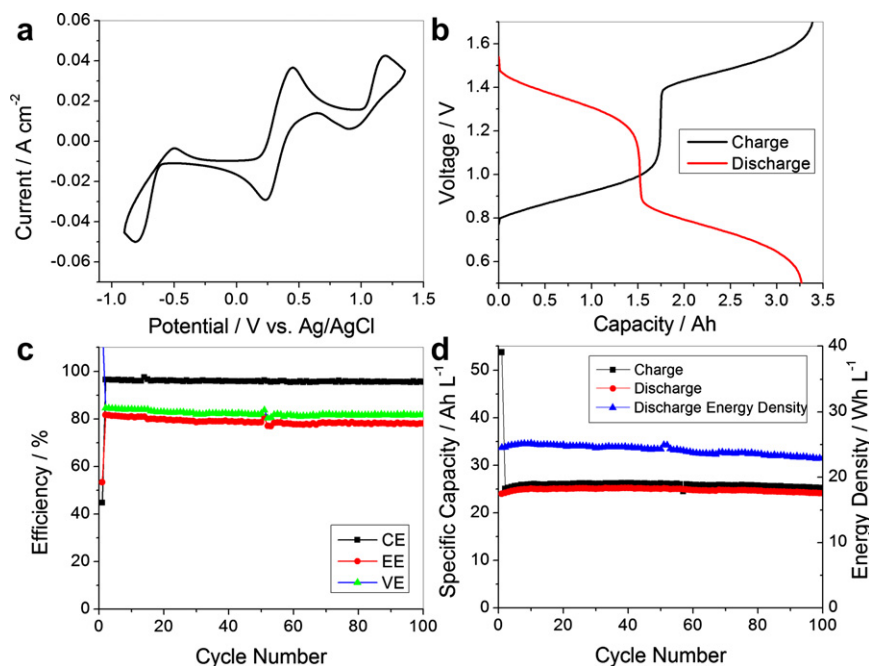


Fig. 1. (a) Cyclic voltammetry (CV) spectrum on glassy carbon working electrode in the 1.5Fe/V/S–6.8Cl electrolyte at 10 mV s⁻¹ scan rate. The electrochemical performance of a Fe/V mixed acid redox flow cell with 1.5Fe/V/S–6.8Cl electrolyte in each half cell and NR-212 as the membrane. (b) Cell voltage profile versus cell capacity during a typical charge/discharge process. (c) Cyclic coulombic efficiency (CE), voltage efficiency (VE), and energy efficiency (EE) as functions of cycle number. (d) Variation of specific volumetric capacity and discharge energy density with cycle number.

Corroborating the CV scan results, two voltage plateaus were observed, as shown in a typical plot of cell voltage versus cell capacity (Fig. 1(b)). The voltage plateau at ~0.9 V during charge and ~0.75 V during discharge corresponds to the Fe²⁺/Fe³⁺ vs. V²⁺/V³⁺ redox couple, while the voltage plateau at ~1.5 V during charge and ~1.35 V during discharge represents the V⁴⁺/V⁵⁺ vs. V²⁺/V³⁺ redox reaction. The voltage profile demonstrated by the Fe/V hybrid flow battery is in good agreement with the previously reported Fe²⁺/Fe³⁺ vs. V²⁺/V³⁺ redox reaction in an Fe/V mixed acid flow cell and V⁴⁺/V⁵⁺ vs. V²⁺/V³⁺ redox reaction in the VRB with mixed acid electrolyte [22,25]. Fig. 1(c) exhibits the efficiencies of the Fe/V hybrid cell with the sulfate–chloride mixed acid electrolyte up to 100 cycles, in which a coulombic efficiency of ~96% and a voltage efficiency of ~83% were achieved, leading to an overall energy efficiency of ~80%. The Fe/V hybrid flow battery also presented excellent capability retention as shown in Fig. 1(d) with no obvious capacity loss throughout the 100 cycles. The discharge energy density, representing the ultimate capability of the cell to deliver useful energy, is also plotted in Fig. 1(d); close to 25 Wh L⁻¹ of specific volumetric energy density was obtained over 100 cycles of electrochemical cycling; (the calculation was based on the total electrolyte volume in both negative and positive half cells). Compared with the Fe/V cell using the sulfate–chloride mixed acid electrolyte, the Fe/V hybrid cell achieved a >60% increase in the specific volumetric energy density attributed to the contribution from the second redox reaction pair. The excellent electrochemical performance of the Fe/V hybrid cell validates our design principle of improving the energy density of a flow battery system by utilizing multiple electron transfer, as was discussed in the Introduction.

In a comparable study, the identical cell and electrolyte were tested with cell voltage window limited to between 1.1 and 1.7 V. Therefore only the V⁴⁺/V⁵⁺ vs. V²⁺/V³⁺ redox couple is utilized in the cell charge/discharge cycling, as shown in Fig. 2. In Fig. 2(a), the voltage plateau at ~1.5 V during charge and ~1.35 V during discharge represents the V⁴⁺/V⁵⁺ vs. V²⁺/V³⁺ redox reaction.

Although a stable energy efficiency of ~85% is achieved over 100 cycles (Fig. 2(b)), cell capacity as well as energy density demonstrated rapid decay over continuous cycling, as shown in Fig. 2(c). In the first five cycles, the flow cell achieved an average energy density of ~23 Wh L⁻¹. It is well known that VRB systems often suffer from substantial capacity loss due to different diffusion rates of the vanadium ions across the membrane disturbing the state-of-charge balance between the two half cells and causing significant capacity decay [26]. By adding an extra redox couple into the cell reaction, the Fe/V hybrid flow battery not only attained a relatively higher energy density, but also exhibited stable capacity over extended cycling, which enables the system to be operated with minimal electrolyte maintenance. It is worth noting that the capacity retention capability of a hybrid redox flow battery can be significantly affected by altering the available active redox couples. A detailed study on the subject could shed light on the capacity fading mechanism of VRB systems.

The electrochemical cycling performance of a Fe/V flow battery utilizing only the Fe²⁺/Fe³⁺ vs. V²⁺/V³⁺ redox couple has been previously reported [24,25], using identical cell configuration and electrolyte composition with a limited voltage window of 0.5–1.35 V. Stable electrochemical cycling performance was successfully demonstrated over 100 cycles with an energy density of ~15 Wh L⁻¹. The major challenge of the Fe/V redox flow battery, however, is its low energy density due to an intrinsically lower cell voltage. Incorporation of the V⁴⁺/V⁵⁺ vs. V²⁺/V³⁺ redox couple into the Fe/V flow battery system significantly increased the average operational voltage of the system, leading to a much improved system energy density; the combination also inherits excellent capacity retention capability from the previous Fe/V system, demonstrating much improved cycling stability compared with the reported vanadium sulfate redox flow battery cycling performance [27–29]. Moreover, in the previous Fe/V system, neither the vanadium ions in the positive electrolyte nor the iron ions in the negative electrolyte participated in the redox reactions during

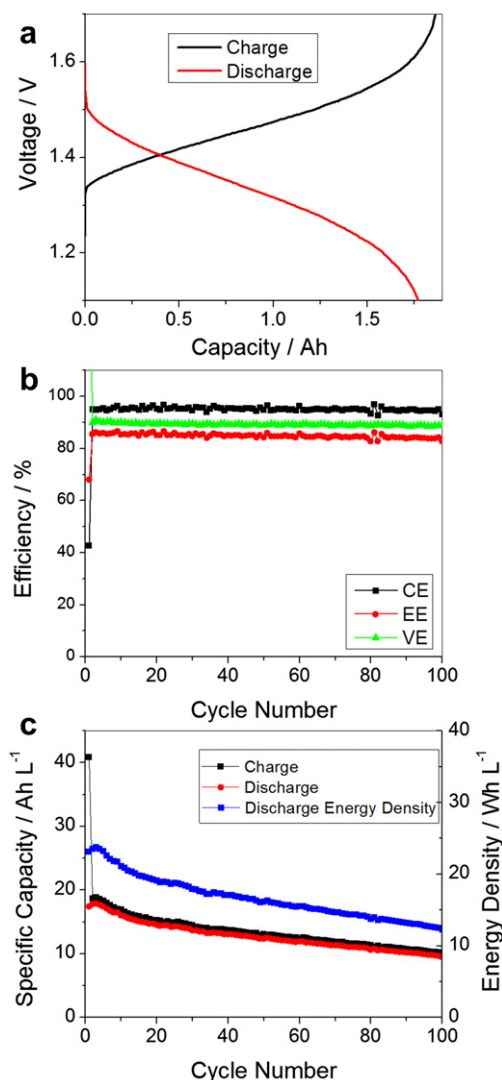


Fig. 2. Cycling performance of a redox flow battery in the voltage window of 1.1–1.7 V using 1.5Fe/V/S–6.8Cl mixed acid electrolyte. (a) Cell voltage profile, (b) efficiencies, (c) capacity change versus cycle number.

cycling. As a result, half of the fuel (redox active ions in the electrolyte) was wasted in terms of contributing to the system energy output. In contrast, by exploiting the V^{4+}/V^{5+} vs. V^{2+}/V^{3+} redox couple, the current Fe/V hybrid system made full use of the positive electrolyte, which resulted in a higher fuel utilization ratio. On the other hand, the Fe/V hybrid system presumably demands high-cost perfluorinated polymer based membrane due to the presence of highly oxidative V^{5+} ions, while the previous Fe/V has demonstrated stable cycling with micro-porous separator. The trade-off between the energy density and the cost of membrane must be considered in the future system development.

Despite the continuous development of the VRB system, its high cost is still a hurdle preventing the VRB system from a broader market penetration. The vanadium electrolyte accounted for ~35% of the capital cost of the VRB system, mainly due to the high and volatile price of the vanadium [20]. From a cost-effectiveness perspective, it is therefore important to compare the different vanadium based redox flow batteries in terms of the energy performance per unit of vanadium source consumed. For this purpose, the energy densities per mole of vanadium of the different vanadium-related redox flow battery systems are listed in Table 1.

Table 1

Discharge energy density per mole of vanadium of the different vanadium-related redox flow batteries at the current density of 50 mA cm^{-2} [22,25].

	VRB	Gen 3 VRB	Fe/V	Fe/V hybrid
Electrolyte composition	1.6V–4.5S	2.5V–6Cl	1.5Fe/V/S–6.8Cl	1.5Fe/V/S–6.8Cl
Energy density/vanadium (Wh (L·M)^{-1})	14.1	15.4	10	16.7

Table 1 shows that the Fe/V hybrid flow battery system achieves the highest value, representing the most efficient use of the vanadium source among the different systems, because of the successful substitution of the V^{4+}/V^{5+} couple with the low-cost Fe^{2+}/Fe^{3+} couple.

In a summary, an aqueous redox flow battery with multi-electron transfer has been successfully demonstrated. Although the advantage of incorporating multi-electron transfer into a redox flow battery was not fully realized due to the lack of available redox couples in the negative electrolyte, a Fe/V hybrid flow battery did deliver a much improved energy density, and provides a sensible way to utilize multiple redox couples in designing flow battery systems with high energy density.

4. Conclusions

A novel redox flow battery system based on V^{4+}/V^{5+} vs. V^{2+}/V^{3+} and Fe^{2+}/Fe^{3+} vs. V^{2+}/V^{3+} redox couples in sulfate–chloride mixed acid electrolytes was successfully demonstrated in a laboratory-scale flow cell. With 1.5 M Fe and 1.5 M V in 1.5 M sulfate and 3.8 M hydrochloric acid solution, the redox flow cell achieved an energy efficiency of ~80% and negligible capacity fading over 100 cycles when employing NR-212 as the membrane. A significant increase in the energy density was accomplished, indicating great potential for developing a high energy density redox flow battery for large-scale energy storage.

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